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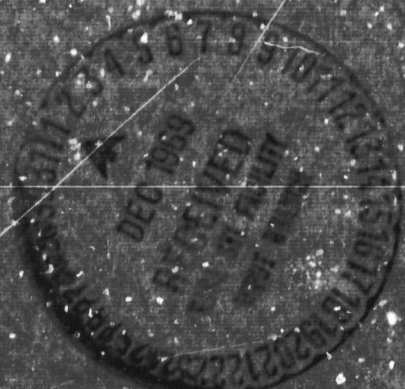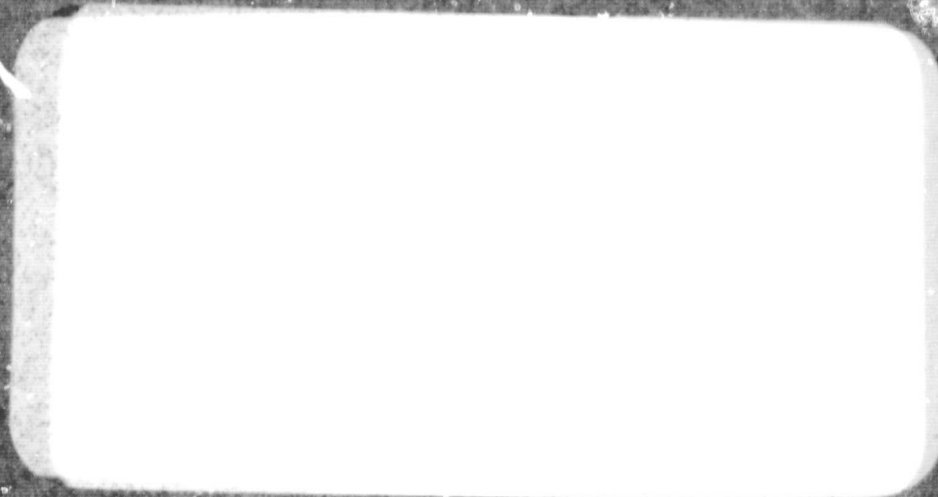
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LOW TEMPERATURE SPECIFIC
HEAT OF VANADIUM CARBIDE

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by

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ABSTRACT

The specific heat has been measured at low temperatures ($\sim$ 1 K to 20 K) for four large crystals of VC_x, with results that indicate the presence of maxima near $x = 0.85$ in both the Debye characteristic temperature, θ_o, and the electronic density of states at the Fermi level $N_\gamma(\zeta)$. The behavior of θ_o suggests that the maximum melting temperature of VC_x occurs at a composition close to that of the ordered compound V_6C_5, rather than at the composition $VC_{0.75}$ proposed recently by Rudy. The variation of $N_\gamma(\zeta)$ with x has been used to obtain an estimate for the density-of-states curve in the vicinity of the Fermi level. The result is discussed in terms of the behavior expected from elementary considerations of the electronic structure.

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§1. INTRODUCTION

Vanadium carbide is one member of a class of materials known as
the refractory hardmetals (Schwarzkopf and Kieffer 1953, Kieffer and
Benesovsky 1963) that is formed by combining a transition metal with one
of the small nonmetal atoms such as boron, carbon, or nitrogen. Although
these materials have been studied extensively in recent years, the origins
of their properties remain obscure. However, interesting correlations
become evident when the refractory hardmetals and the transition metals are
compared with respect to the manner in which their properties depend on
the position of the transition element in the periodic table (Brewer and
Krikorian 1955, 1956a, 1956b; Dempsey 1963). These similarities have
suggested that the principal components of the bonding in the refractory
hardmetals are related more closely to the metal-metal interactions of
the transition metals than to the metal-nonmetal interactions of the
common transition metal compounds (Kiessling 1957, Robins 1958). Support
for this assumption has been provided by Lye and Logothetis (1966); who
employed measurements of the optical reflectivity in conjunction with the
LCAO formalism of Slater and Koster (1954) to calculate an electronic
energy band structure for TiC. The result exhibited a close resemblance
to the electronic structure of fcc transition metals (Lye 1967), and indi-
cated that electrons were transferred from the 2p states of the carbon
atom to crystalline energy bands derived from the 3d states of the metal
atom, as had been suggested earlier by Umanskii (1943). This transfer of
electrons between states of different symmetries compensates only partially

for the negative charge deposited within the carbon atom spheres by the overlap of electronic wave functions associated with the metal atoms. Indeed, if the relative displacements of the 2p and 3d bands of TiC (Lye and Logothetis 1966) and VC (Lye, Hollox and Venables 1968) are attributed solely to the Madelung potential of point ions, it is necessary to assign a net <u>negative</u> charge of approximately 0.3 e to the carbon atoms and an equal positive charge to the metal atoms. The contribution to the cohesion due to this partially ionic bond appears to be small, amounting to less than 10% of the total cohesive energy, the remainder arising from the formation of electronic energy bands with low-lying states derived primarily from the atomic states of the metal atom.

An alternative description (Rundle 1948) of the refractory hardmetals is based on the assumption that the bonding is contributed predominantly by strong covalent interactions between the metal and nonmetal atoms. This point of view has been supported by the results of an earlier LCAO calculation of the electronic structure of TiC (Bilz 1958) and more recent APW calculations (Ern and Switendick 1965, Conklin and Silversmith 1968). These band structures indicate that a major portion of the bonding arises from interactions between the 2p-orbitals of the carbon atoms, and from hybridization interactions between these orbitals and the 3d-orbitals of the metal atoms. Moreover, the energy bands derived from the 2p-states of the carbon atom lie sufficiently low that some electrons are transferred to them from the 3d-states of the metal atom, i.e., opposite to the direction of transfer indicated by the electronic structure of Lye and Logothetis.

These differences reflect the uncertain knowledge of the correct electronic constitution of the refractory hardmetals, and indicate the need for additional experimental data. Appropriate information has been scarce in the past because of the difficulties encountered in growing usefully large single crystal specimens of these highly refractory materials. The problem is complicated by the fact that many of the refractory hardmetals exhibit an unusually broad range of homogeneity, within which their properties vary with the concentration of the nonmetal atom. The observed behavior is, therefore, sensitive to the degree of uniformity in the composition of the specimen studied. However, when suitably homogeneous materials are available, this variation can be exploited to investigate the manner in which the nonmetal atoms influence the electronic structure. A variety of such studies have been made on sintered powders (c.f. Bittner and Goretzki 1962, 1963), but relatively little work has been done with well-characterized crystals. Recently, however, large crystals of vanadium carbide have been prepared at RIAS using a floating zone technique and zone levelling to obtain uniform composition (Precht and Hollox 1968).

Studies of the crystal structure (Venables, Kahn, and Lye 1968), mechanical behavior (Lye et al. 1968, Hollox and Venables 1968) and radiation damage (Venables and Lye 1969) of certain of these crystals have been reported previously. The present investigation has been concerned with the low temperature specific heat of VC_x crystals, and with the interpretation of the experimental observations in terms of the

electronic structure near the Fermi level. The specimens and the experimental techniques employed in this study are described briefly in §2. The results are presented and discussed in terms of the electronic structure of VC in §3.

§2. EXPERIMENTAL

2.1. Specimen Characterization.

Crystalline boules of VC_x were prepared as 1.3 cm diameter rods, 0.5 to 1.5 g mole in size, using the methods described by Precht and Hollox (1968). Approximately uniform compositions were achieved by using as a starting charge material having the composition of the liquidus at the melting point of the desired crystalline product (Pfann 1952, 1966). A narrow molten zone was formed first in the starting charge. This zone was then passed slowly into and along a dense, sintered rod of composition close to that of the crystalline solid freezing out simultaneously at its trailing edge. The accuracy of this method is limited somewhat by vaporization losses, and by uncertain knowledge of the phase diagram (Storms and McNeal 1962). Consequently, the crystalline boules usually exhibited small gradations in composition from one end to the other.

Detailed chemical analyses have been performed only on representative boules, to avoid excessive consumption of the crystalline product. Usually, the material examined in this manner contained approximately 0.01 w/o each of oxygen and nitrogen, as well as traces of metallic impurities. The carbon-to-metal, C/V, atom ratios, x, of most specimens

have been estimated from measurements of their X-ray lattice parameters using the data compiled by Storms (1967). On this basis, the difference in composition, δx, between opposite ends of the rod was less than 0.01 for all the samples discussed here.

The nominal composition, x, ascribed to each sample was established by using the average of the compositions determined from the lattice parameters measured at each end of the rod. One specimen, $VC_{0.85}$, was found to have a carbon-to-metal atom ratio within the range in which the ordered compound V_6C_5 is expected to occur (Venables et al. 1968). The existence of this ordered structure in this specimen was confirmed by observing its optical anisotropy in reflected polarized white light. Another specimen exhibiting almost the same lattice parameter was estimated from NMR data to have x = 0.84. Thus, this method of specifying the composition may be subject to systematic errors in x of approximately 0.01.

2.2. Sample Mounting, Thermometry, and Specific Heat Measurements.

The four samples were measured in the same holder, which consisted of a 0.1 mm thick copper foil formed and soldered to a cylindrical shape, carrying a Manganin wire heater and a calibrated germanium resistance thermometer. The holder could be connected to a mechanical heat switch, and was well isolated from vibration and radiation (Lowndes and Finegold 1969a, Lowndes, Finegold, Rogers and Morosin 1969). The

calibration of the thermometer 2.3-20 K is referred to the National
Bureau of Standards acoustic scale T_{65} (Plumb and Cataland 1966), and
below 2.3 K is referred to the ^{4}He vapor-pressure scale T_{58} (Brickwedde,
Van Dijk, Durieux, Clement and Logan 1960). Constant temperatures were
maintained in the helium bath during the calibration by using an elec-
tronic regulator described previously (Venegas and Finegold 1969). Specific
heat measurements were made using the usual heat-pulse method (Nernst 1910,
Eucken 1909, Cochran, Shiffman and Neighbor 1966), with temperature incre-
ments chosen to hold systematic errors in the lattice specific heat to
less than 0.1% (Hoare, Jackson and Kurti 1961). Thermometer and heater
currents were kept very stable (Lowndes and Finegold 1969b) and measured
by low-voltage d.c. techniques (5-dial potentiometer: Leeds and Northrup,
Philadelphia, Penna., U.S.A.; nanovolt detector: Keithley 147, Cleveland,
Ohio, U.S.A.). The heat capacity of the holder was measured separately.
Measurements (Bloom, Lowndes and Finegold 1969) of the specific heat of
a sample of Calorimetry Conference Standard Copper and of National Bureau
of Standards copper of residual resistivity ratio 30,000 (Powell, Clark
and Fickett 1969) are in good agreement with those of Osborne, Flotow
and Schreiner (1967), giving confidence that the absolute accuracy of the
specific heat measurements is within 1%. However, the intra-laboratory
precision of the comparison of the specific heat of the VC_x samples is
well within 1%.

§3. RESULTS AND DISCUSSION

Figures 1 and 2 show the specific heat, C, of the four samples of VC_x plotted as C/T versus T^2[†]. The data points for each sample were fitted by the least squares method, with $1/C^2$ weighting, to equations of the form

$$C = \gamma T + \alpha T^3 + \beta T^5 \qquad (0 - 5 \text{ K}),$$

$$\text{and} \qquad C = \gamma T + \alpha T^3 + \beta T^5 + \delta T^7 \quad (0 - 20 \text{ K}),$$

both of which yielded practically the same values for the coefficients of T and T^3. From the coefficients γ and α determined by this procedure, the electronic density of states, $N_\gamma(\zeta)$, and the Debye characteristic temperature, θ_o, were determined using the relations

$$N_\gamma(\zeta) = \gamma[3/2\pi^2 k_B^2 N_A]$$

$$\text{and} \qquad \theta_o^3 = [(12/5)\pi^4 N_A k_B]/\alpha,$$

in which $N_\gamma(\zeta)$ is the electronic density of states at the Fermi surface for a single spin orientation, expressed here in terms of a formula unit, VC_x, containing one vanadium atom, k_B is Boltzmann's constant, and N_A is Avogadro's number. The results are summarized in table 1.

[†] The data for $VC_{0.87}$ and $VC_{0.75}$ departed from the smooth curve expected at temperatures below 1.73 K and 1.87 K, respectively. The behavior suggests the onset of superconductivity in either the sample or some constituent of the holder. These data points have been omitted from figs. 1 and 2. The original specific heat data are available on request from L. F. Additional studies of the superconducting properties of VC_x will be performed in co-operation with the Cryogenics Division, National Bureau of Standards, Boulder, Colo.
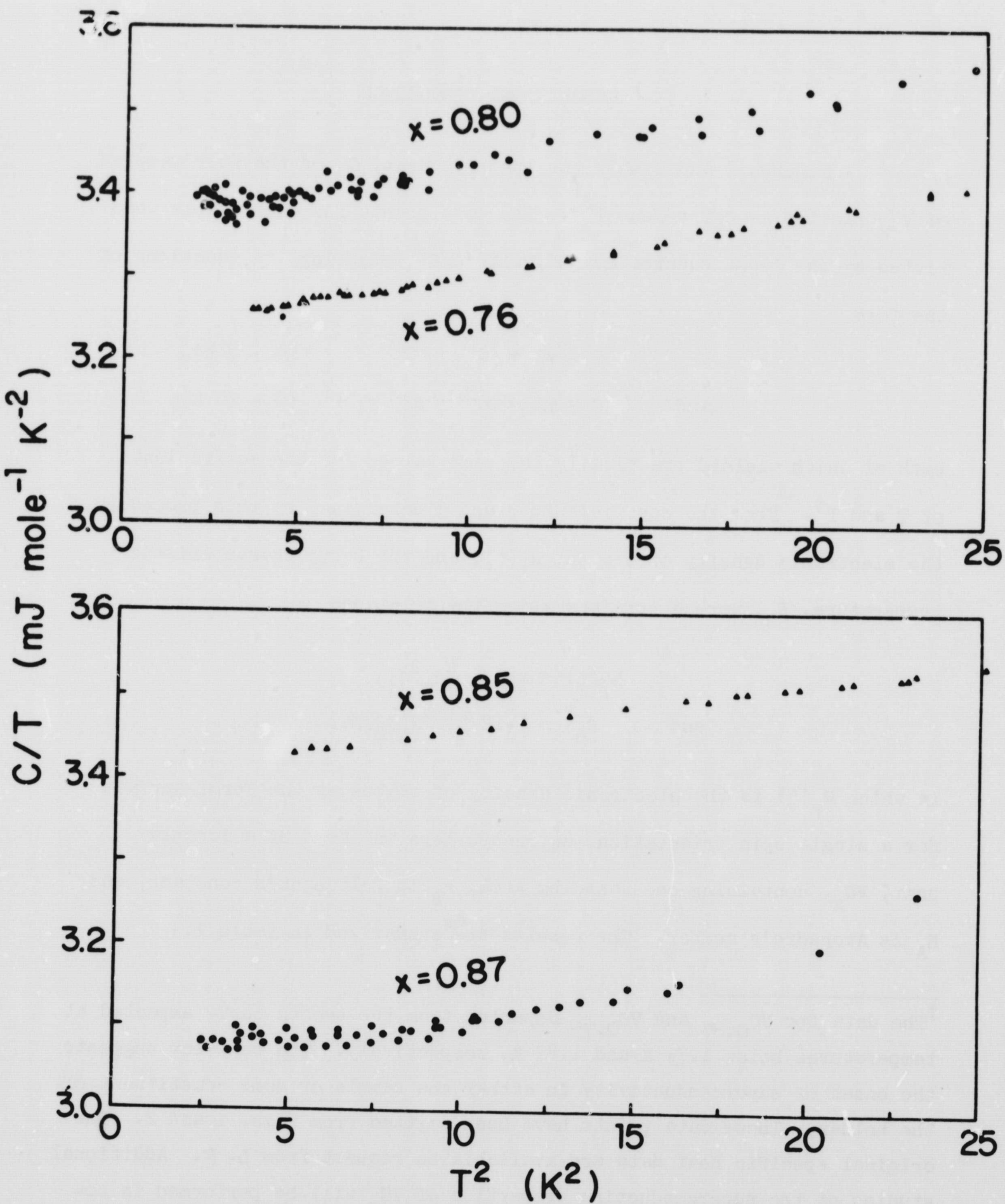
Figure 1. The specific heat of VC_x in the temperature range 0-5 K, plotted as C/T versus T^2.
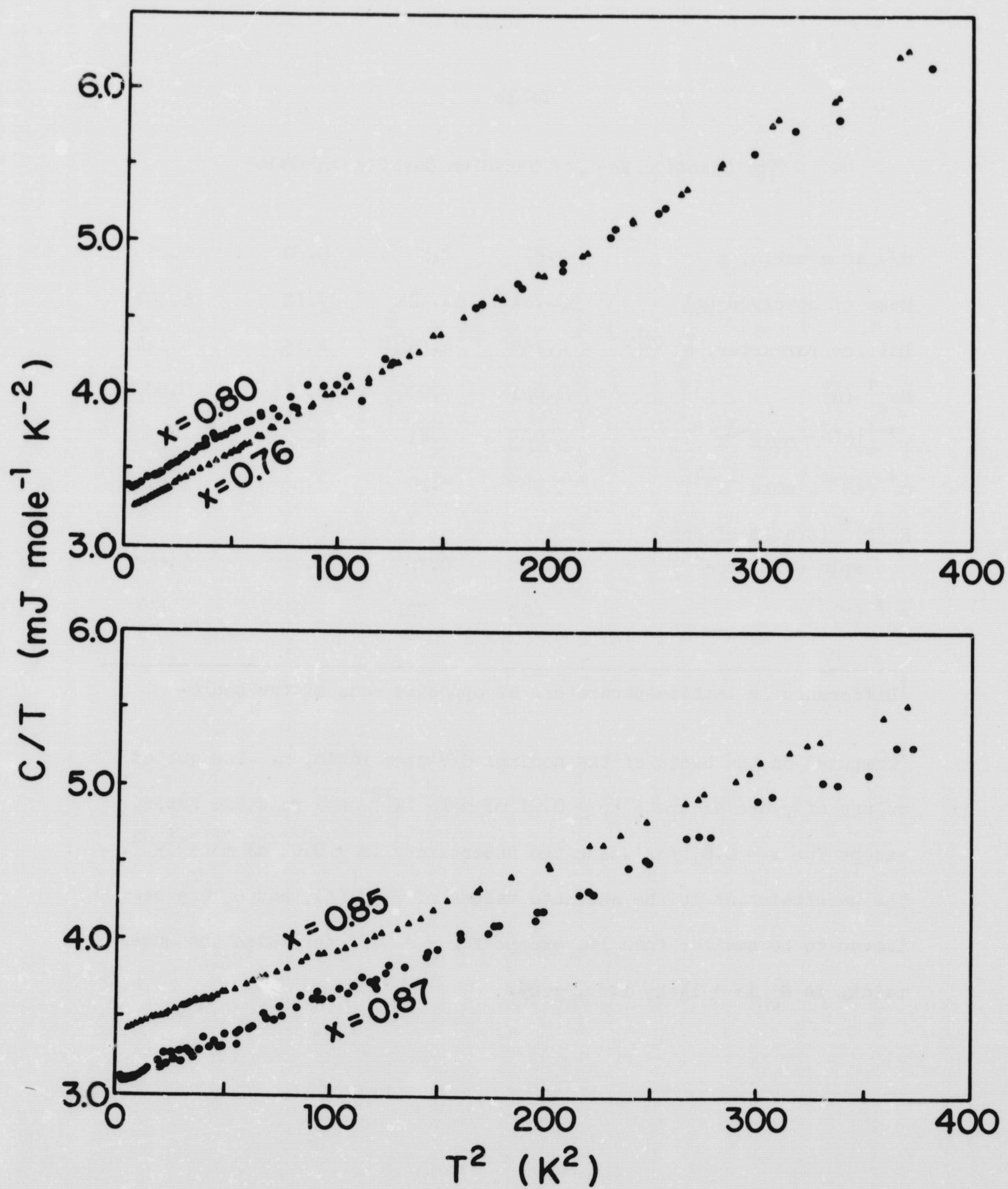
Figure 2. The specific heat of VC_x in the temperature range 0-20 K, plotted as C/T versus T^2.

Table 1

The Specific Heat of Vanadium Carbide Crystals

C/V atom ratio, x	0.87	0.85	0.80	0.76
Mass of specimen (g)	30.714	62.423	59.129	86.001
Lattice parameter, $\bar{a}_o$ (Å)	4.165	4.162	4.151	4.134
δa_o[†] (Å)	0.001	0.0005	0.003	0.002
γ[‡] (10^{-3} J mole^{-1}K^{-2})	3.06	3.41	3.36	3.23
α[‡] (10^{-6} J mole^{-1}K^{-4})	5.78	5.19	7.55	7.61
$N_\gamma(\zeta)$[‡] (states of one spin eV^{-1} atom^{-1})	0.648	0.723	0.712	0.685
θ_o[‡] (K)	690	721	636	635

[†]Difference in lattice parameters at opposite ends of the boule.

[‡]Computed on the basis of the nominal C/V atom ratio, x. The quoted values of γ are accurate to ± 0.01 mJ mole^{-1}K^{-2} on a relative basis, except for $x = 0.87$ for which the uncertainty is ± 0.02 mJ mole^{-1}K^{-2}. The uncertainties in the absolute values of γ, $N_\gamma(\zeta)$, and θ_o are believed to be smaller than 1%, except for $x = 0.87$ for which the uncertainty in θ_o is ± 14 K, i.e., $\pm 2\%$.

It may be noted that both θ_o and $N_\gamma(\zeta)$ assume their greatest values at the nominal composition x = 0.85. If the Lindemann (1910) melting formula is applicable to these materials, this variation in θ_o is consistent with the phase diagram of the V-C system published by Storms (1967), and with qualitative observations of the melting behavior during growth of these crystals (Precht 1968). On the same basis, the variation of θ_o observed here disagrees with the phase diagram proposed by Rudy (1969), in which the maximum melting temperature occurs at a much lower carbon content, near the composition $VC_{0.75}$. More detailed investigations will be required to resolve this question, but the present results suggest that the maximum in the melting curve for the nominally cubic VC phase occurs in the ordered compound V_6C_5.

Behavior somewhat similar to that exhibited by θ_o is observed also in the variation of $N_\gamma(\zeta)$ with x. Following the procedure suggested by Hoare, Matthews and Walling (1953), this dependence on composition of the density of states at the Fermi level can be used to obtain an estimate of the variation of the density of states with energy for a fixed composition. Thus, if n electrons are transferred from each carbon atom to the energy bands derived from atomic states of the metal atom, the displacement, ΔE, of the Fermi level caused by a change in composition from x_1 to x_2 is given by

$$\Delta E = \frac{n}{2} \int_{x_2}^{x_1} dx/N(\zeta).$$

The results of this calculation are plotted in fig. 3, using an energy scale normalized with respect to the number of electrons transferred.

This approach may be expected to yield a useful approximation to the density-of-states curve so long as the Fermi level is not displaced by large amounts, and the electronic structure is not altered drastically as the composition is changed. It appears likely that both restrictions are satisfied in VC_x (and TiC_x). For example, if the number of electrons transferred is assumed to be near unity (Lye 1965, Lye and Logothetis 1966), the Fermi level moves by only 0.1 eV as x varies from 0.76 to 0.87. Moreover, severe distortions of the energy bands are not expected, because elementary considerations of the electronic structures of TiC and VC (Lye and Logothetis 1966, Lye et al. 1968) suggest that the prominent features near the Fermi level in their density-of-states curves are determined primarily by energy bands derived from the 3d-states of the metal atoms. Although these energy bands can be expected to move slightly in energy as the composition is changed, the dominant characteristics of the peaks will remain, and the Fermi level will be established relative to these peaks according to the total number of electrons available.

Indeed, a peak similar to the one observed was expected to be present near the Fermi level of VC from the previous considerations of its electronic structure (Lye et al. 1968). Like the peak shown in fig. 3
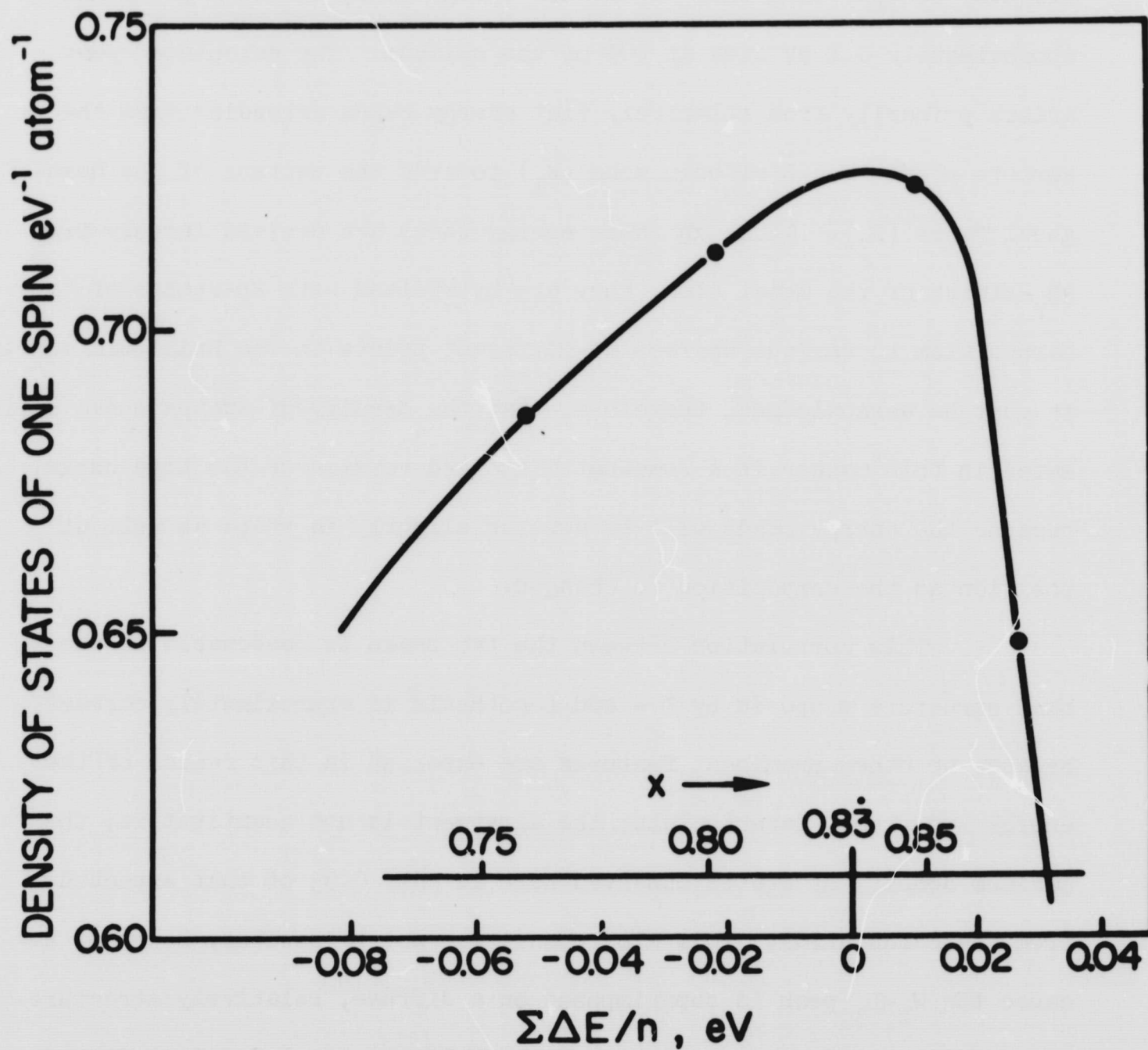
Figure 3. The electron density-of-states curve near the Fermi level of VC_x as derived from the specific heat by the method of Hoare et al. (1953). The zero of energy is chosen arbitrarily at the Fermi level of V_6C_5 ($VC_{0.833}$).

the calculated peak is asymmetrical, with the edge at high energies slightly steeper than that on the low energy side, and both peaks are approximately 0.1 eV wide at 90% of the maximum. The calculated peak arises primarily from relatively flat energy bands extending from the corners of the fcc Brillouin zone (W_1) towards the centers of the hexagonal faces (L_3). Although these energy bands are derived largely from $3d_\gamma$-states of the metal atom, they are hybridized with 2p-states of the carbon atom to various degrees at different points in the Brillouin zone. It must be acknowledged, therefore, that the density-of-states curve estimated in this manner is a somewhat distorted version of the true curve, because the energy bands will be altered slightly in shape as well as position as the composition is changed.

This correlation between the two peaks is reasonable if the band structure proposed by Lye and Logothetis is approximately correct, because no other prominent features are expected in this region of the energy spectrum. Nevertheless, the agreement is not quantitative; the maximum density of states observed here is only 0.53 of that expected from the calculation. This discrepancy may not be serious, however, because the W_1-L_3 peak is superimposed on a diffuse, relatively structureless background that contributes almost half the total density of states near this energy. Small changes in the LCAO band parameters may permit a redistribution of these states without introducing new peaks, but more sophisticated calculations of the electronic structure would be required

to resolve the question unambiguously. Unfortunately, recent calculations using the augmented plane wave (APW) method (Ern and Switendick 1965, Conklin and Silversmith 1968) have not yet provided a resolution in the density-of-states curve sufficiently detailed to permit comparison with these experimental data.

The influence of ordering in the carbon sublattice (De Novion, Lorenzelli and Costa 1966; Froidevaux and Rossier 1967, Venables et al. 1968) has been neglected in this discussion, because the metal sublattice, which appears to dominate the electronic structure, is only slightly distorted from the fcc configuration. Thus, the extended zones of the ordered compounds will deviate from the fcc Brillouin zone primarily by the presence of small band gaps on certain interior planes. Only those band gaps that occur very close to the Fermi level will influence the electronic specific heat, but even these usually will introduce only small changes because the perturbation in the energy bands extends over only a very limited volume of the Brillouin zone. Although these interior band gaps may not be observable in the electronic specific heat or in other physical parameters that are obtained from sums over the complete Brillouin zone, it is anticipated that certain of them will be detectable in the modulated reflectance spectra of the ordered compounds.

§4. SUMMARY AND CONCLUSION

Measurements of the low temperature specific heat of VC_x have provided estimates of the Debye characteristic temperature, θ_o, and of the density of states, $N_\gamma(E)$, near the Fermi level. The maximum value

of θ_o occurs at a composition close to that of the ordered compound V_6C_5, which suggests that the maximum melting temperature in the VC phase may also occur in this compound.

The density-of-states curve obtained from these studies exhibits a narrow peak which is similar to one expected near the Fermi level of VC_x from elementary considerations of the electronic structure. If this correlation is valid, it supports the suggestion that electrons are transferred _from_ states associated with the carbon atoms _to_ energy bands derived from atomic states of the metal atom. Moreover, it establishes the position of the W_1 electronic state within the band structure at an energy near the Fermi level of V_6C_5. However, positive confirmation must await more refined calculations and more detailed experimental studies.

The compositional variation in the density of states at the Fermi level of VC_x inferred from the present study of the specific heat differs from that expected from prior measurement of the magnetic susceptibility (Bittner and Goretzki 1962). Part of the discrepancy may arise from many-body enhancement effects that modify the two parameters by different amounts, but it appears possible that differences in specimen preparation may also be a contributing factor. In an effort to resolve this question, portions of the crystalline boules employed in this study of the specific heat are now being used also for measurements of the magnetic susceptibility and superconducting transition temperature.

ACKNOWLEDGEMENTS

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